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Mechanical Properties of Unsaturated Polyester / Montmorillonite Composites

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ABSTRACT

Nanocomposites composed of unsaturated polyester matrix and organically modified clay filler were prepared. After the synthesis, XRD patterns showed that the interlayer spacing expanded from 1.25 nm to 4.5 nm. The mechanical properties of the nanocomposites were determined and it was found that adding only 3 w/w % organically modified clay improved the flexural modulus of unsaturated polyester by 35%. From DSC diagrams, it was found that T_g values of the nanocomposites also increased with the clay content. It is concluded that partially exfoliated / intercalated nanocomposites were formed at relatively low clay contents.

INTRODUCTION

Nanocomposites with thermoplastic matrices have been synthesized and characterized [1-4]. Several studies have also been reported on nanocomposites with thermoset matrices. Lee and Jang [5] reported the characterisation of epoxy-clay hybrid composites prepared by emulsion polymerization. The effects of promoter and curing process on exfoliation behavior of epoxy/clay nanocomposites were studied by Ke, Lü, Yi, Zhao and Qi [6]. Kornmann, Linberg and Berlung [7] synthesized epoxy clay nanocomposites and analysed the nature of the curing agent on structure. Kornmann, Berglund and Giannelis [8] studied nanocomposites based on montmorillonite modified with silane coupling agent and unsaturated polyester. In the present study, the type and content of the montmorillonite (MMT) on mechanical and thermal properties are investigated using an unsaturated polyester (UP) matrix.

EXPERIMENTAL

Organically treated montmorillonite (Cloisite® 30B from Southern Clay Products, USA) and non-treated Na-montmorillonite (Cloisite® Na⁺ from Southern Clay Products, USA) were used as the filler. Ortho-phthalic-general purpose unsaturated polyester (Neoxil C-92 N 8 from Camelyaf, Turkey) was used as the matrix. The resin and the matrix were first mixed mechanically for 3 hours at 50°C followed by ultrasonic mixing for better dispersion. 0.9 phr of methyl ethyl ketone peroxide (MEK-P) and 0.2 phr of cobalt naphthanate (as 8 % solution) were used as the catalyst and accelerator respectively.

Flexural tests were performed according to the Test Method-I Procedure A of ASTM D790-92 using Lloyd 30k Universal Testing Machine with a crosshead speed of 2.8 mm / min. Pendulum Charpy Impact Tests were done according to the Test Method-I Procedure A in ASTM D256-91a using a Coesfeld Material device. In order to evaluate changes in T_g with increasing clay content, differential scanning calorimeter analyses were carried out using General

V4.1C DuPont 2000. Fracture surfaces were investigated by using JEOL JSM-6400 Scanning Electron Microscope (SEM). The fracture surfaces of pure UP and specimens containing MMT were compared. X-Ray diffraction patterns were recorded by monitoring the diffraction angle 2θ from 1° to 10° using a Rigaku Geigerflex diffractometer.

RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of organoclay Cloisite® 30B. The diffraction peak appears at $2\theta = 4.4^\circ$, with basal spacing of 1.97 nm. The original Na^+ -montmorillonite gives basal spacing of 1.25 nm. [4]. In Figure 2, it can be seen that the peak corresponding to the basal spacing of organoclay has disappeared. It is clearly shown that for all the samples with Cloisite® 30B a new diffraction peak appeared at $2\theta = 2^\circ$ with a basal spacing of 4.5 nm. However, if the organoclay loading is greater than 3%, the hybrids also show a small peak at $2\theta = 4.93^\circ$ ($d = 1.93$ nm), which is the main peak of the organoclay, suggesting that a small part of organoclay is not dispersed at the molecular level.

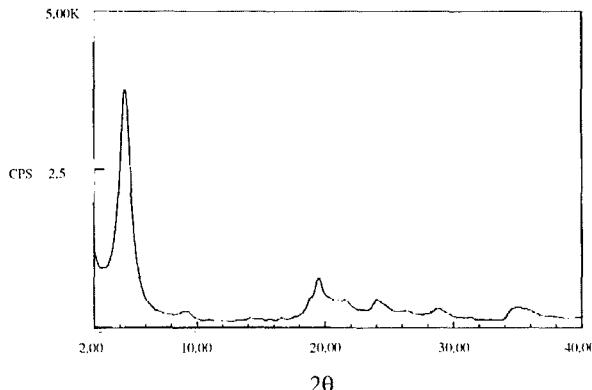


Figure 1: X-Ray pattern of Cloisite® 30B

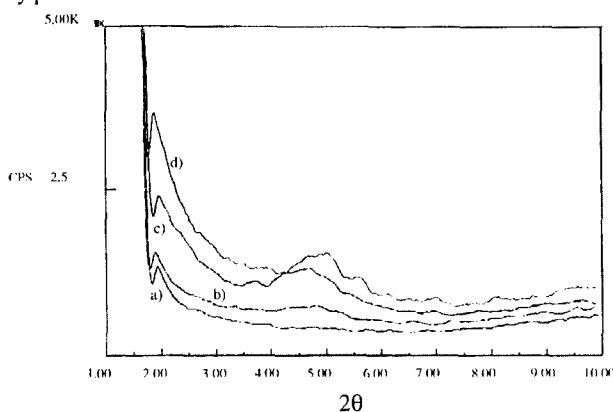


Figure 2: X-Ray patterns of nanocomposites a) 3%, b) 5%, c) 7%, d) 10% filler

Figure 3 shows the effect of the clay content on the T_g . Since the glass transition process is related to the molecular motion, the increase in the T_g of the nanocomposites, in comparison with the original unsaturated polyester, can be attributed to high degree of adhesion between the polymer and the layered silicate surfaces. The nanometer size restricts segmental motion near the organic-inorganic interface. However, the clay particles also consume free radicals that are formed during curing, thus the cross-link density might decrease at high clay contents suggesting that the glass transition might also decrease at high clay contents.

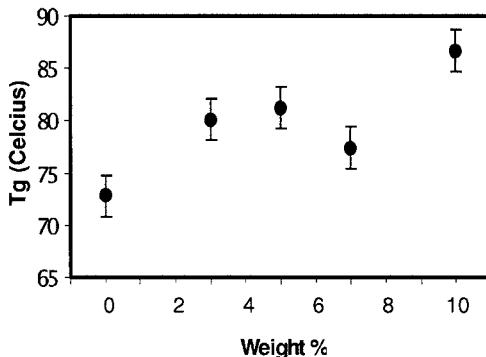


Figure 3: T_g results of samples with Cloisite® 30B or Na^+

As can be seen from Figure 4, flexural modulus increases and makes a peak at 3% loading of Cloisite® 30B. With respect to the clay content, the increase in flexural modulus is more than the increase in tensile modulus (not shown here). The tensile modulus of unsaturated polyester was improved by 17% at 5% of Cloisite® 30B. The orientation of the clay particles may be substantially parallel to the mold surface and this leads to high flexural modulus values. After 7% of loading, there is a decrease in the modulus. At high loading levels, polymer-clay interactions are lower and agglomeration of the clay particles results in lower modulus. The cross-link density might also be lower at high clay contents as discussed earlier, leading to lower modulus. In Cloisite® Na^+ samples, the increase in flexural modulus is not significant owing to lack of intercalation of the polymer chains in between the clay layers.

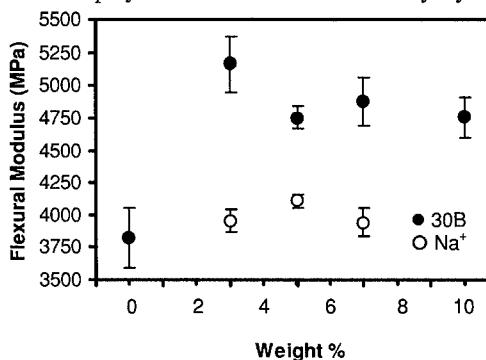


Figure 4: Flexural modulus versus weight % values of Cloisite 30B and Na^+ samples

As can be seen from Figure 5, at high Cloisite® 30B content, flexural strength of the specimens decrease, since the clay particles act as stress concentrators and intercalation is poor at high filler contents. The flexural strength of Cloisite® Na^+ samples also decreases. In this case, the clay particles, which are in the agglomerate form, act as stress concentrators and tend to decrease the flexural strength of the specimens.

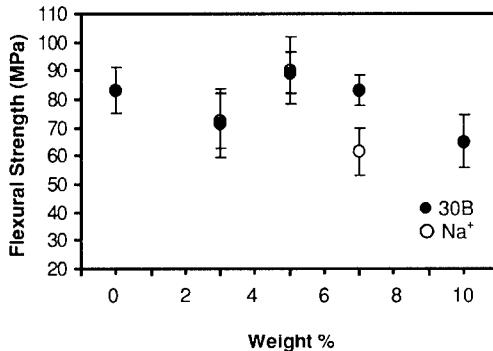


Figure 5: Flexural strength versus weight % values of Cloisite 30B and Na^+ samples

The strain at break values decrease for both types of samples with respect to the clay content, since the elongation is born by the decreasing quantity of matrix at high filler contents (Figure 6).

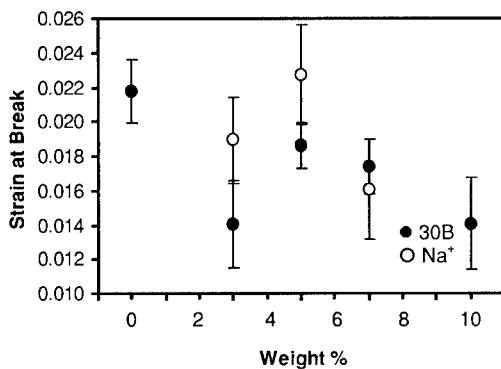


Figure 6: Strain at Break versus weight % values of Cloisite 30B and Na^+ samples

As far as the impact behavior is concerned (Figure 7), clay particles act as a crack initiator, but at high clay contents the particles also act as crack stoppers. Impact values of Cloisite® Na^+ show that unmodified clay particles have no positive effect on the composite, because the narrow d-spacing of the clay, do not permit the polymer to enter between the galleries leading to agglomeration of the particles and lower impact strength values.

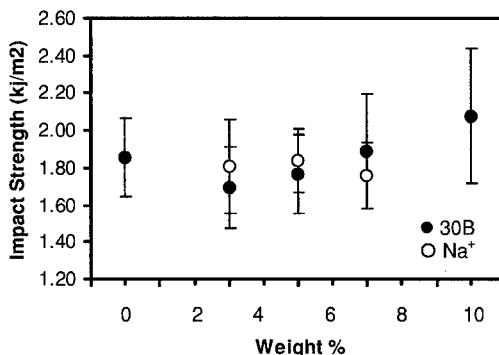


Figure 7: Impact strength values of Cloisite® 30B and Na⁺ samples

As can be seen from Figures 8 and 9, the size of the agglomerates found in the samples containing Cloisite® Na⁺ are larger then the samples containing Cloisite® 30B. In Figure 9, it is seen that the quantity of the agglomerates is higher, and the impact energy is lower owing to the higher quantity of particles.

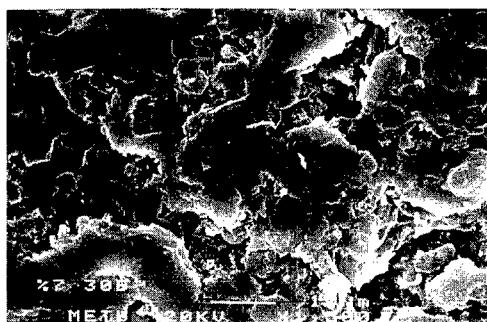


Figure 8: Impact surface of 7 % Cloisite® 30B sample at x1500 magnification



Figure 9: Impact surface of 7 % Cloisite® Na⁺ sample at x1500 magnification

CONCLUSIONS

Addition of an organoclay (Cloisite® 30B) in relatively low ratios, to an unsaturated polyester resin resulted in partially exfoliated nanocomposites. From XRD patterns, it is concluded that the d-spacing of the organoclay expanded from 1.97 nm to 4.5 nm in all samples with Cloisite® 30B. T_g values of the samples containing Cloisite® 30B increased from 72°C, in unfilled unsaturated polyester, to 86°C in 10% Cloisite® 30B loaded unsaturated polyester.

The flexural modulus of the samples containing Cloisite® 30B increased by 35% at 3% clay loading. Flexural strength decreased at high clay contents and the strain at break values changed in the opposite manner to the flexural modulus. The flexural modulus of specimens containing Cloisite® Na^+ exhibit a maximum of 3829 MPa at 5% clay loading, resulting in an increase of only 7%. The impact values of the samples containing Cloisite® 30B first decreased and then, started to increase. However, in samples containing Cloisite® Na^+ , the values of the impact strength showed continual decrease with respect to clay content.

From Scanning Electron Microscope, it was seen that there are large agglomerates in the samples containing Cloisite® Na^+ type of clay leading to poor mechanical properties. With the help of the X-Ray analysis, it is concluded that the dispersion of the Cloisite® 30B montmorillonite particles is good and the silicate particles near the primary particles are exfoliated.

REFERENCES

- [1] A. Okada, M Kawasumi, Ausuki, Y. Kojima, T. Kurauchi, and O. Kamgaito, "Nylon 6-clay Hybrid", *Mater. Res. Soc. Proc.*, 171, 45-50 (1990)
- [2] Richard A. Vaia, Klaus D. Jandt, Edward J. Kramer and E. P. Giannelis, "Kinetics of Polymer Melt Intercalation", *Macromolecules*, 28, 8080-8085 (1995)
- [3] X. Fu, Squubuddin, "Polymer-clay Nanocomposites: Exfoliation of Organophilic Montmorillonite Nanolayers in Polystyrene", *Polymer*, 42, p: 807-813 (2001)
- [4] T. Agag, T. Koga, T. Takeichi, "Studies on Thermal and Mechanical Properties of Polyimide-clay Nanocomposites", *Polymer*, 42, p: 3399-3408 (2001)
- [5] Dong Choo Lee, Lee Wook Jang, "Characterization of Epoxy-clay Hybrid Composite Prepared by Emulsion Polymerization", *Journal of Applied Polymer Science*, Vol. 68, 1997-2005 (1998)
- [6] Y. Ke, Jiankun Lü, X. Yi, J. Zhao, Z. Qi, "The Effects of Promoter and Curing Process on Exfoliation Behavior of Epoxy/clay Nanocomposites", *Journal of Applied Polymer Science*, Vol. 78, 808-815 (2000)
- [7] X. Kornmann, H. Lindberg, L. A. Berglund, "Synthesis of Epoxy-clay Nanocomposites. Influence of the Nature of the Curing Agent on Structure", *Polymer*, 42, p: 4493-99 (2001)
- [8] X. Kornman, L. A. Berglund, J. Sterte and E. P. Giannelis, "Nanocomposites Based on Montmorillonite and Unsaturated Polyester", *Polymer Engineering and Science*, V38 No:8 p: 1351-1358 (1998)